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A Molecular Orbital Study on the Interaction Between BF$_3$ and the Compounds Dimethyl Ether and Perfluorodimethyl Ether

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A MOLECULAR ORBITAL STUDY ON THE INTERACTION BETWEEN BF$_3$ AND THE COMPOUNDS DIMETHYL ETHER AND PERFLUORODIMETHYL ETHER

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ABSTRACT

A molecular orbital method was used to study the interaction between BF$_3$ (a Lewis acid) and the compounds dimethyl ether and perfluorodimethyl ether. The results indicated the existence of a Lewis acid-base interaction between the BF$_3$ molecule and dimethyl ether but no interaction with the perfluorodimethyl ether. In addition, the results of a second molecular orbital study, involving the interaction between AlF$_3$ (another Lewis acid) and perfluorodimethyl ether, also indicated no Lewis acid-base interaction.

INTRODUCTION

Many researchers (refs. 1 to 4) have investigated the high temperature catalytic decomposition of perfluoropoly-alkylethers (PFPEs) in the presence of metal oxides and metal fluorides in order to explain, and hopefully prevent, PFPE degradation under tribological conditions. Two viewpoints have emerged concerning the decomposition mechanism. Some reseachers (refs. 1, 2, and 5) have postulated that the surface Lewis acid sites of certain metal oxides and metal fluorides attacked the oxygen lone-pair electrons of the PFPEs initiating decomposition. Other researchers (refs. 3, 6, and 7), however, have conducted experiments suggesting that these surface Lewis acid sites may not be involved in the decomposition of PFPEs.

Ball and Zehe (ref. 8) added support to the latter viewpoint by conducting infrared matrix-isolation spectroscopy studies on the interaction between BF$_3$ (a strong Lewis acid) and the model compounds (C$_2$H$_5$)$_2$O and (C$_2$F$_5$)$_2$O. Their findings confirmed the known Lewis acid-base interaction between BF$_3$ and the diethyl ether but no observable interaction with the perfluorodiethyl ether. The possibility, however, was raised that infrared-active vibrations due to BF$_3$-perfluorodiethyl ether interaction may have been too weak for detection under the co-condensed conditions of the matrix isolation apparatus.

A computational molecular orbital (MO) study on the interaction between BF$_3$ and two model compounds, dimethyl ether (DME) and perfluorodimethyl ether (PFDE), was undertaken to hopefully reproduce (computationally) the experimental results of Ball and Zehe, using two similar but smaller model ether molecules. The interaction between AlF$_3$, another Lewis acid, and PFDE was also studied since the catalytic decomposition of PFPEs by AlF$_3$ at elevated temperatures is known to occur (ref. 1).

MODEL COMPOUNDS AND COMPUTATIONAL DETAILS

The AM1 self-consistent field molecular orbital procedure developed by Dewar and co-workers was used in this study. Although ab initio methods can be used for these small molecules, it is our intent to study the behavior of very long chain perfluoro ether molecules in the near future. The use of ab initio methods would become prohibitively time consuming and calculationally expensive for these exceedingly large molecules. It was thus decided to employ semiempirical methods (AM1 or PM1) for current and future work.

The computations employed in this study used the HyperChem version 4.0 of AM1 using the RHF option on a 486DX personnel computer. Complete geometric optimization during energy minimization was performed for all single molecules and for all interacting pairs of molecules. Configuration interaction was not used. Computing times ranged from 1 to about 8 hr.

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RESULTS AND DISCUSSION

Before computational runs were performed on the interaction between the ether molecules and the Lewis acid molecules, two preliminary tests of the AM1 program were made. The first test compared the calculated proton affinity of the perfluorodimethyl ether molecule, using the AM1 program, with the proton affinity calculated using <u>ab initio</u> methods. The second test involved the analysis of the computational results between the interaction of NH_3 and BF_3.

First Test

An initial molecular geometric structure for PFDE was obtained using the model builder routine of the semi-empirical program (fig. 1(a)). Figure 1(b) shows the optimized molecular structure and atomic charges of PFDE as predicted by the AM1 method. Table I lists the calculated bond lengths, angles, and dihedral (or torsion) angles of this molecule and compares them to the calculated values obtained by other researchers using RHF/3-21G (ref. 9) and RHF/4-31G (ref. 10) <u>ab initio</u> methods. The experimental values (ref. 10) are also listed. The bond lengths and angles calculated using the AM1 method are less than 3 percent greater than the experimental values. Both the AM1 and <u>ab initio</u> results are in excellent agreement with the experimental results. The dihedral angle predicted by AM1 was 1.4° greater than the experimental value of 164°.

Vibrational analysis of the AM1 optimized structure revealed no negative frequencies indicating this was indeed a valid minimun energy structure.

The optimized PFDE molecule was then protonated by interacting H^+ with the O atom of the ether molecule. Figure 2 shows the optimized protonated ether molecular structure. Vibrational analysis revealed no negative frequencies. Table II lists and compares the bond lengths and angles with the values obtained by the RHF/3-21G <u>ab initio</u> method (ref. 9). Proton affinity (PA) is defined as the energy given off when a molecule accepts a proton in the gas phase:

$$M + H^+ \rightarrow MH^+ \qquad \Delta H \equiv \text{proton affinity} \qquad (1)$$
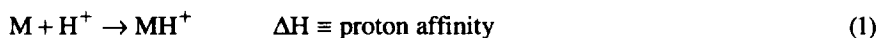
The proton affinity can thus be calculated using heats of formation in the following equation:

$$\Delta H_{rxn} = \Delta H_f(MH^+) - \Delta H_f(M) - \Delta H_f(H^+) \qquad (2)$$

where:

Proton Affinity (PA) = $-\Delta H_{rxn}$
ΔH_f of Protonated Perfluorodimethyl ether (MH$^+$) = -671.8 kJ/mol (this work)
ΔH_f of Perfluorodimethyl ether (M) = -1592.7 kJ/mol (this work)
ΔH_f of H$^+$ = 1537.4 kJ/mol (experimental value)

The PA value calculated using equation 2 was 616.4 kJ/mol compared to the PA value of 585.5 kJ/mol calculated by Fontaine et al. (ref. 9). The AM1 PA result was thus only 5 percent greater than the <u>ab initio</u> PA result.

Second Test

A computational run was then performed on the interaction between BF_3 and NH_3. NH_3 is a molecule that interacts strongly with surface Lewis acid sites and is widely used as a poison to block the effect of these sites. Optimized geometries are shown in figure 3 and total energy values are listed in table III. Henceforth, only select distances and angles will be reported.

The B-N distance was 1.782 Å, and the net atomic charges on the BF_3 and NH_3 groups were ±0.326 respectively. The calculated dihedral angle of the BF_3 group, $-130.7°$, showed this molecule was distorted from its normal planar trigonal geometry. The NH_3 bond angles increased form 109.1° to 111.4° and the dihedral angle increased from

119.0° to 125.0°. The total energy of the BF_3—NH_3 system was 52.2 kJ/mol lower than the added total energy of the isolated molecules. The HOMO orbital plot for this system is shown in figure 4. One can notice a withdrawal of the nitrogen 2p orbital toward the boron atom.

These results indicated that an adduct was formed between BF_3 and NH_3 which is what one would expect experimentally.

Perfluoro ether Results

(1) BF_3 Interactions

The first two calculations involved the interaction between BF_3 and the O atom of a dimethyl ether molecule and the perfluorodimethyl ether molecule. The optimized structure and total energy for the BF_3—$(CH_3)_2O$ system are shown in figure 5 and table III. Vibrational analysis of this system revealed no negative frequencies. The distance between the boron atom and the ether oxygen atom was 1.905 Å. The net atomic charge on the BF_3 group was –0.119, and the charge on the dimethyl ether was +0.119. The geometry of the BF_3 group was not planar trigonal as noted its dihedral angle of 159.4°. The total energy of the BF_3—$(CH_3)_2O$ system was 30.4 kJ/mol lower than the added total energy of the isolated molecules. The HOMO orbital plot for this system showed withdrawal of the oxygen 2p orbital toward the boron atom.

The computed vibrational infrared frequencies, for the BF_3—$(CH_3)_2O$ adduct, can be compared (see table IV) with the experimental values determined by Hunt and Ault (ref. 11). Very good agreement was observed with the two experimental frequencies assigned to the antisymmetric B—F stretching vibrations (1260 cm^{-1} and 1221 cm^{-1}) and with the frequency assigned to the B—O stretching vibration (624 cm^{-1}). The computed frequency corresponding to the symmetric B—F stretching vibration (812 cm^{-1}), however, was not observed.

The optimized structure and total energy of the BF_3—$(CF_3)_2O$ system are shown in figure 6 and table III. Vibrational analysis revealed no negative frequencies. The distance between the boron atom and the ether oxygen atom was 3.594 Å. The net atomic charge on the BF_3 group was zero as well as on the ether group. The geometry of the BF_3 group was planar trigonal as noted by its dihedral angle of 179.8°. The total energy of this system equaled the added total energy of each isolated molecule. The HOMO orbital plot for this system showed no withdrawal of the oxygen 2p orbital towards the boron atom.

A third calculation was performed interacting BF_3 with one of the fluorine atoms (the one with the most negative atomic charge) of the perfluorodimethyl ether molecule. The distance between B and the F atom was 3.557 Å. The net atomic charges on the BF_3 and ether groups were both zero. The geometry of the BF_3 molecule was planar trigonal as noted by the computed angles. The total energy of this system was 0.3 kJ/mol higher than the added total energy of each isolated molecule.

The last computation involved the interaction between AlF_3 and the perfluorodimethyl ether molecule at the oxygen atom of the ether. The distance between the O and Al atoms was 4 Å. The net atomic charges on the AlF_3 and ether groups were both zero. The geometry of the AlF_3 molecule was planar trigonal, and the total energy of this system was 1 kJ/mol higher than the added total energy of each isolated molecule.

These results support the existence of a Lewis acid-base interaction between the BF_3 and dimethyl ether molecules, but no Lewis acid-base interaction between the BF_3 and perfluorodimethyl ether molecules. These computational results are in agreement with the experimental observations of Ball and Zehe (ref. 8). In addition, interaction between the perfluorodimethyl ether and AlF_3, another Lewis acid, was not noted. Although the presence of the metal atoms of a metal oxide or metal fluoride cannot be ruled out as a contributing factor in the high temperature decomposition of PFPEs, this molecular orbital study does suggest that the formation of a classical Lewis acid-base adduct, like that of the BF_3—NH_3 system, will not occur between PFPE molecules and surface Lewis acid sites.

CONCLUSIONS

Results of this AM1 semi-empirical molecular orbital study showed the formation of a classical Lewis acid-base adduct between dimethyl ether and BF_3. The formation, however, of a Lewis acid-base adduct between perfluorodimethyl ether and BF_3 (as well as AlF_3) was not observed, thus confirming the experimental work of Ball and Zehe. Therefore, these results indicate that the high temperature catalytic decomposition of PFPEs is not due to surface Lewis acid sites but to other unknown sites. Future work will focus on identifying these sites.

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TABLE I.—PERFLUORODIMETHYL ETHER RESULTS

Bond length, Å	HF/3-21G basis	HF/4-31G basis	AM1 this work	Experimental
$(C_1\text{-}O)$, $(C_2\text{-}O)$	1.370	1.369	1.405	1.369
$(C_1\text{-}F_1)$, $(C_2\text{-}F_4)$	1.322	1.331	1.351	1.327
$(C_1\text{-}F_2)$, $(C_2\text{-}F_5)$	1.331	1.342	1.353	1.327
$(C_1\text{-}F_3)$, $(C_2\text{-}F_6)$	1.337	1.347	1.354	1.327
Bond angles, °				
$C_1\text{-}O\text{-}C_2$	124.1	125.9	121.3	119.1
$F_1\text{-}C_1\text{-}O$	108.0	107.6	104.8	---
Dihedral angle, °				
$F_1\text{-}C_1\text{-}O\text{-}C_2$	---	162.0	165.4	164

TABLE II.—PROTONATED
PERFLUORODIMETHYL ETHER
RESULTS

Bond length, Å	HF/3-21G basis	AM1 this work
C_1-O	1.508	1.521
H-O	.989	.992
C_1-F_1	1.305	1.333
C_1-F_2	1.301	1.331
C_2-F_4	1.304	1.333
Bond angles, °		
C_1-O-C_2	123.0	128.5
F_1-C_1-O	103.9	101.9

TABLE III.—TOTAL ENERGY CALCUALTIONS (kJ/mol)

Molecule	Total energy	System	Total energy
BF_3	−147,795.2	BF_3/NH_3	−171,849.4
NH_3	−24,002.0	BF_3/DME	−211,489.7
AlF_3	−145,947.0	BF_3/PFDE	−484,789.4
DME	−63,664.1	AlF_3/PFDE	−482,940.1
PFDE	−336,994.1	− − − − − −	− − − − −

DME—Dimethyl ether
PFDE—Perfluorodimethyl ether

TABLE IV.—COMPUTED VIBRATIONAL
INFRARED FREQUENCIES FOR THE
BF_3—$(CH_3)_2O$ ADDUCT

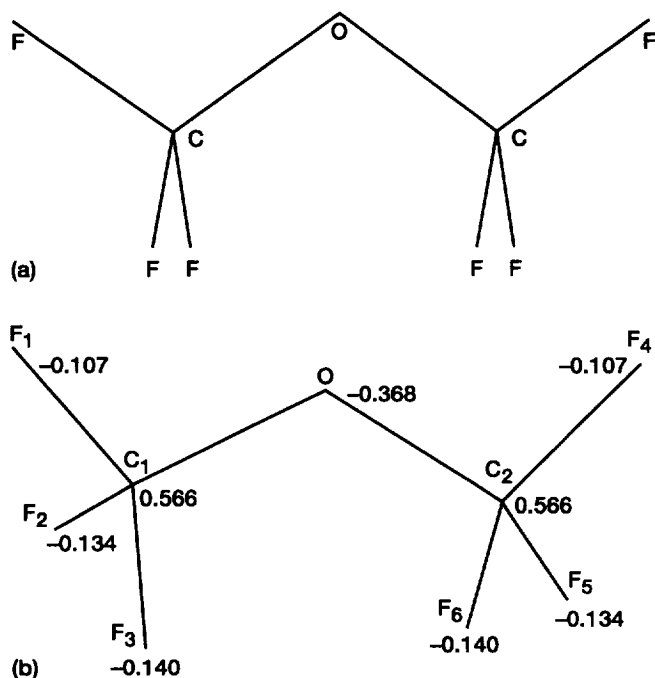| AM1 this work	Experimental	Assignment
1329 cm^{-1}	1260 cm^{-1}	ASYM B-F str.
1205	1221	ASYM B-F str.
− − − − −	812	SYM B-F str.
637	624	B-O str.

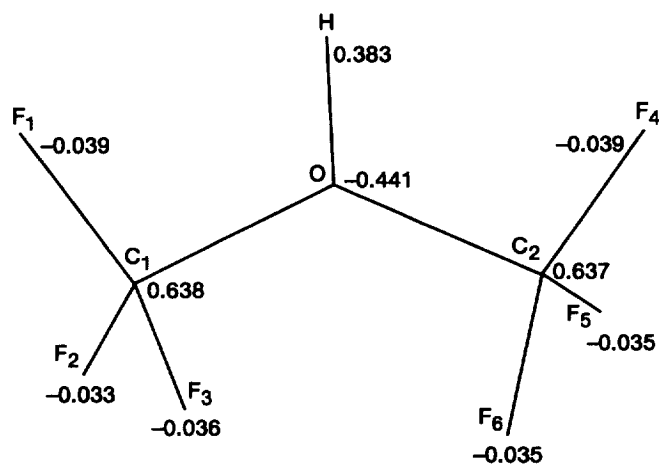Figure 1.—(a) Initial molecular structure for PFDE. (b) Optimized molecular structure for PFDE.

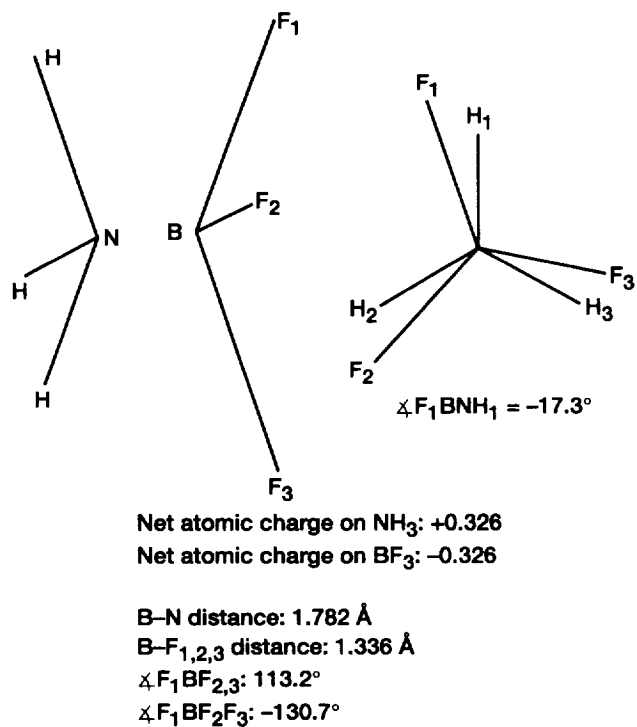Figure 2.—Optimized molecular structure for protonated PFDE.

$\angle F_1BNH_1 = -17.3°$

Net atomic charge on NH_3: +0.326
Net atomic charge on BF_3: -0.326

B–N distance: 1.782 Å
B–F$_{1,2,3}$ distance: 1.336 Å
$\angle F_1BF_{2,3}$: 113.2°
$\angle F_1BF_2F_3$: -130.7°

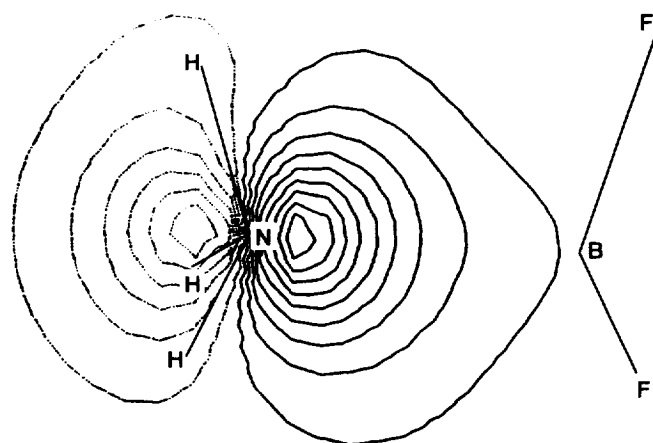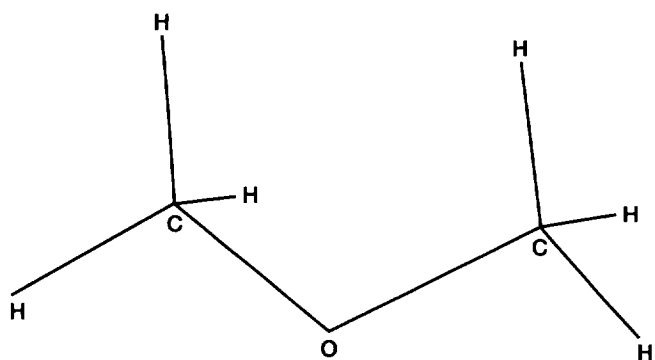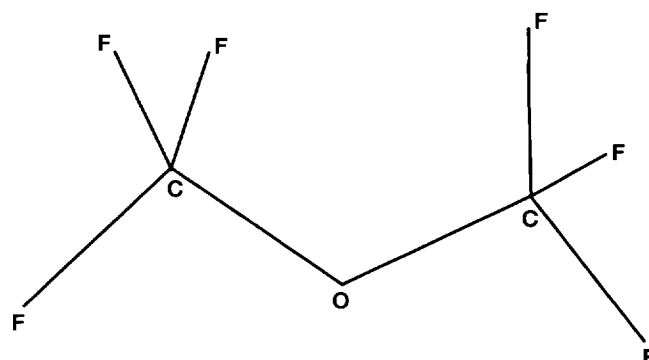Figure 3.—Optimized molecular interaction between BF_3 and NH_3.

Figure 4.—HOMO orbital plot for BF_3–NH_3 interaction.

Net atomic charge on DME: +0.119
Net atomic charge on BF_3: –0.119

B–O distance: 1.905 Å
$\angle F_1BF_2$: 119.0°
$\angle F_1BF_2F_3$: 159.4°

Figure 5.—Optimized molecular interaction between DME and BF_3.

Net atomic charge on PFDE: 0
Net atomic charge on BF_3: 0

B–O distance: 3.594 Å
$\angle F_1BF_{2,3}$: 120.0°
$\angle F_3BF_2F_1$: 179.8°

Figure 6.—Optimized molecular interaction between PFDE and BF_3.

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